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13. ABSTRACT *(Maximum 200 words)*

This research project addressed several aspects of the surface chemistry of electronic materials. COF_2 was shown to be an effective thermal and photochemical etchant of Si and SiO_2. A general purpose molecular beam scattering apparatus was constructed to investigate the mechanism of COF_2 etching of Si. H_2 and CH_4 scattering from the Fe(111) surface was studied in order to characterize the operation of this system. Dynamics of van der Waals bound clusters interacting with solid surfaces were investigated. Deposition of metallic layers from organometallic precursors was also studied.

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MECHANISMS OF REACTIVE ETCHING

Final Technical Report
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Period: 5/1/85-6/30/89

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Professor of Chemistry
Principal Investigator

The following pages describe the results of work funded by the Air Force Office of Scientific Research under grant number AFOSR-85-0209G. The title of this program is "Mechanisms of Reacting Etching," and it covers the period from May 1, 1985 to June 30, 1989. Work during this time period resulted in the publication of seven papers acknowledging AFOSR support, with one more currently in press, and three additional manuscripts in preparation. These papers are listed in Table 1. Our research has proceeded along four lines during the funding period. These are described individually in what follows.

A. Interaction of COF_2 with Si(111).

The original objective of our work was to develop an understanding of the mechanism of reactive etching of silicon surfaces. In order to address this question, studies of the interaction of COF_2 with the Si(111) and SiO_2 surface were carried out. A single crystal Si(111) surface was cleaned and characterized by LEED and Auger electron spectroscopy in an ultra-high vacuum surface analysis chamber. The sample was then mounted in a separate UHV system attached to a quadrupole mass spectrometer for thermal desorption studies. The sample was cleaned according to the procedure established by LEED/AES studies, and then exposed to COF_2.

Heating initiated reaction of the adsorbed COF_2 with the Si(111), and desorbed product species. Significant quantitites of SiF_4 were detected in the thermal desorption product, indicating that COF_2 was an active etchant of the Si(111) surface. These results suggested that divalent and trivalent adsorption sites on the Si(111) (7x7) surface might be especially active for the adsorption and dissociation of COF_2, resulting in the etching of the surface. It was also found in these studies that SiO_2 surfaces could be etched by COF_2 when the COF_2 was irradiated with IR photons from a CO_2

laser. Infrared multiphoton absorption by the COF_2 probably results in the cleavage of the C-F bond, forming F· and COF· radicals. Since SiO_2 is relatively inert to atomic fluorine etching, the observed etching reaction likely proceeds through adsorption of the COF· radical and subsequent breaking of the Si-O bond. Fluorination of the Si then occurs via decomposition of the adsorbed COF, and SiF_4 eventually is desorbed from the surface. This work is described in paper 1 of Table 1.

B. Inelastic Scattering of N_2 and CH_4 from Fe(111).

In order to carry out more detailed investigations of the mechanism of COF_2 interacting with the Si(111) surface, construction of a multiple purpose molecular beam scattering apparatus was initiated early in the grant period. This system is designed to probe inelastic and reactive interactions of molecules with well-characterized surfaces. The translational energy of the incident molecules can be varied, and the system is designed so that state specific excitation of the incident beam molecules is possible. Angular distributions and time of flight measurements on the scattered molecules can be carried out as well. This apparatus has been characterized by inelastic scattering studies of N_2 and CH_4 from the clean Fe(111) surface as a function of incident molecule velocity. This work is described in detail in papers 8, 9 and 10 of Table 1.

A very interesting change in angular distribution of scattered N_2, from a broad, nearly cosine distribution at low scattering energies, to a narrow, directed distribution at higher energies has been observed for N_2 scattering from the Fe(111) surface. Calculational modeling of the N_2/Fe(111) scattering, including stochastic trajectory calculations to model these distributions have been carried out in order to help to provide an interpretation of this unusual change in scattering behavior with velocity.

It is possible that this change in scattering behavior is related to the energy dependent increase in the dissociative sticking probability of N_2 on the Fe(111) surface observed by Rettner and coworkers.[2] The experimental aspects of this work have been presented at the Campobello Island conference on surface interactions in August 1989, and will appear as part of the conference proceedings (Paper 8, Table 1). The modelling aspects of the work and a more detailed description of the experimental results are currently being prepared (Paper 9, Table 1).

In addition to detailed studies of N_2 scattering from the Fe(111) surface, inelastic scattering of CH_4 from this surface was also investigated. Angular distributions of the scattered CH_4 as well as time-of-flight measurements were carried out. A potential for the CH_4/Fe(111) interaction was obtained by comparison of the measured angular and TOF distributions with modelling calculations as in the N_2/Fe(111) work. This interaction potential includes an attractive well and a corrugation which effectively models the open Fe(111) surface. This work is described in detail in paper 10 of Table 1.

C. N_2 Van der Waals Cluster Scattering

During the construction of the general purpose molecular beam scattering apparatus described in detail in paper 11 of Table 1, studies of N_2 Van der Waals clusters interacting with solid surfaces were carried out. The experimental measurements[3] were carried out using electron beam induced fluorescence in a small scattering apparatus, while the experimental apparatus described above was under construction. Angular distributions and the rotational energy of scattered N_2 cluster fragments resulting from the collision of N_2 Van der Waals clusters with well characterized silver and iron surfaces were measured. The measured angular distributions are

characterized by tangent-shifted scattering lobes, which are essentially independent of angle of incidence, cluster incident energy, and surface conditions. The rotational energy of the scattered nitrogen molecules was found to be greatest at detection angles normal to the surface, but lower in the tangent-shifted scattering lobe.

These experimental results have been interpreted by reference to the results of stochastic trajectory calculations for Argon clusters scattering from Pt(111) surfaces.[4,5] This model system was chosen since the energetics of binding in the Ar clusters are similar to the N_2 cluster situation, and because previous work on the Ar/Pt interaction has provided an accurate interaction potential. Detailed studies of the trajectories of small Ar clusters colliding with the Pt(111) surface suggest that the scattering dynamics are controlled by gas-surface followed by gas-gas binary collision events. These collisions result in the tangent peaked scattering distributions observed experimentally. These studies also indicate that the trapping fraction increases markedly with cluster size, and that trapped cluster fragments are often quite mobile on the surface. Both of these observations help to explain the high quality epitaxial films which are observed to grow under cluster beam epitaxy conditions.[6]

Investigation of larger cluster scattering dynamics indicates the pronounced tangent peaking which is characteristic of cluster break-up upon collision with the surface. These large cluster calculations also help to rationalize the observed rotational energies of the scattered N_2 fragments, with molecules scattered normal to the surface leaving from the upper layer of the colliding cluster, experiencing fewer molecule-molecule collisions which would rotationally cool the scattered molecules. The results of these experimental and theoretical investigations are described in more detail in

papers 3, 4, and 6 of Table 1.

D. Deposition of Metallic Films from Organometallic Precursors

This AFOSR grant has also supported work in the related area of electronic materials surface chemisty concerning the deposition of metallic overlayers on semiconductor surfaces. The mechanism of thermal and photo-assisted deposition of molybdenum on silicon, molybdenum, and copper surfaces has been investigated.[7] This deposition occurs via the decomposition of $Mo(CO)_6$ on the surface. Thermal desorption spectroscopy, x-ray photoelectron spectroscopy, and low energy electron diffraction were used in these studies. In this work a cleaned and characterized Si(100) surface at 110K was exposed to gas phase $Mo(CO)_6$. The surface was then heated slowly (1K/min) while recording x-ray photoelectron spectra. The Mo 3d region of the spectrum shows a sharp transition at around 165K which indicates the initiation of decomposition of the adsorbed carbonyl. On the Si(100) surface, an intermediate unsaturated Mo carbonyl species is observed, which further decomposes to leave Mo on the surface in the presence of carbon and oxygen. If the adsorbed $Mo(CO)_6$ layer is UV irradiated with light from a N_2 laser, or from a broad band mercury lamp, new CO desorption peaks appear in the thermal desorption of the layer, as well as significant changes in the chemical state of the deposited layer as indicated by the x-ray photoelectron spectra. This work is described in detail in papers 2 and 7 of Table 1.

Research supported by AFOSR grant 85-0209G, "Mechanisms of Reactive Etching" has addressed a number of related problems in electronic materials surface chemistry. Construction of a multiple purpose molecular beam scattering apparatus has been completed during this grant period. This instrument is capable of extracting detailed information about inelastic

surface scattering and about the mechanisms and dynamics of heterogeneous reactions. It has been used to investigate the interaction of N_2 and CH_4 with the Fe(111) surface. In addition, studies of COF_2 interaction with the Si(111) surface suggest that COF_2 is an effective thermal and photochemical etchant of the silicon surface. N_2 Van der Waals cluster scattering studies carried out with AFOSR support have elucidated the dynamics of cluster break-up on collision with the surface and have indicated mechanisms for the growth of high quality thin films from cluster beam sources. Deposition of metallic thin films from organo-metallic precursors has also been investigated during the support period.

Table 2 lists professional personnel associated with this research, including degrees awarded and thesis titles. Table 3 lists the invited seminars and papers presented by the principal investigator describing work supported by this grant.

References

1. R. J. Holland, and S. L. Bernasek, J. Appl. Phys. 60, 2553 (1986).
2. C. T. Rettner and H. Stein, J. Chem. Phys. 87, 770 (1987); Phys. Rev. Lett. 59, 2768 (1987).
3. R. H. Holland, G.-Q. Xu, J. Levkoff, A. Robertson, Jr., and S. L. Bernasek, J. Chem. Phys. 88, 7952 (1988).
4. G.-Q. Xu, S. L. Bernasek and J. C. Tully, J. Chem. Phys. 88, 3376 (1988).
5. G-Q. Xu, R. J. Holland, S. L. Bernasek and J. C. Tully, J. Chem. Phys. 90, 3831 (1989).
6. T. Takagi, I. Yamada and A. Sasaki, J. Vac. Sci. Technol. 12, 1128 (1975).
7. C.-C. Cho and S. L. Bernasek, J. Vac. Sci. Technol. A5, 1088 (1987). C.-C. Cho and S. L. Bernasek, J. Appl. Phys. 65, 3035 (1989).

Table 1

Papers Published Acknowledging AFOSR Support

1. "Thermal and Photochemical Promotion of Silicon Etching by Carbonyl Difluoride," R. J. Holland and S. L. Bernasek, J. Appl. Phys, 60, 2553 (1986).
2. "Summary Abstract: The Adsorption and Decomposition of Molybdenum Hexacarbonyl on Mo and Si Surfaces," J. Vac. Sci. Technol. A5, 1088 (1987).
3. "Stochastic Trajectory Studies of Small Argon Cluster Scattering from Pt(111)," G.-Q. Xu, S. L. Bernasek and J. C. Tully, J. Chem. Phys. 88, 3376 (1988).
4. "Experimental Studies of the Dynamics of Nitrogen Van der Waals Cluster Scattering from Metal Surfaces," R. J. Holland G.-Q. Xu, J. Levkoff, A. Robertson, Jr., and S. L. Bernasek, J. Chem. Phys. 88, 7952 (1988).
5. "UHV Transport System for Laser Irradiation Studies," A. L. Helms, Jr., W. A. Schiedt, S. L. Bernasek and B. M. Biwer, Rev. Sci. Instrum., 59, 1223 (1988).
6. "Dynamics of Cluster Scattering from Surfaces," G.-Q. Xu, R. J. Holland S. L. Bernasek and J. C. Tully, J. Chem. Phys., 90, 3831 (1989).
7. "Molybdenum Deposition from the Decomposiion of Molybdenum Hexacarbonyl," C. C. Cho and S. L. Bernasek, J. Appl. Phys. 65, 3035 (1989).
8. "Inelastic Scattering of N_2 from Fe(111)," M. Ruggio, L. Chu and S. L. Bernasek, Applied Physics A, in press.
9. "Translational Energy Dependent Scattering of N_2 from Fe(111): Angular and time-of-flight distribution measurements," L. Chu, M. Ruggio, and S. L. Bernasek, manuscript in preparation.

10. "Energy Dependent Scattering of CH_4 from Fe(111)," L. Chu, M. Ruggio, and S. L. Bernasek, manuscript in preparation.

11. "Design and Implementation of a Multiple Purpose Molecular Beam Surface Scattering Apparatus," L. Chu, A. Robertson, Jr., M. Ruggio, R. Holland, J. Levkoff and S. L. Bernasek, manuscript in preparation.

Table 2

Personnel associated with AFOSR Grant 85-0209G

1. Alexander Robertson, Jr. Ph.D. 1985

   "Molecular Beam Studies of the Interaction of Nitrogen Molecules with the Fe(111) Surface."

   Presently, Member of Technical Staff, AT&T Bell Laboratories, Engineering Research Center.

2. Richard J. Holland Ph.D. 1986

   "Surface Chemical Etching and the Dynamics of Cluster Scattering from Metal Surfaces"

   Presently, Staff Scientist, BASF Wyandotte

3. Chih-Chen Cho Ph.D. 1987

   "Surface Modification by Metal Deposition and Laser Irradiation"

   Presently, Research Scientist, Texas Instruments, Central Research Laboratories

4. Guo-Qin Xu Ph.D. 1987

   "Dynamics of Cluster Scattering from Surfaces"

   Presently, Postdoctoral Associate with Professor J. Polanyi, University of Toronto

5. Michael J. Ruggio PhD. 1989

   "The Dynamics of Nitrogen and Argon Scattering from Fe(111)"

   Presently, Research Chemist, Rohm and Haas Company

6. Dr. Che-Chen Chang, Postdoctoral Associate, 1988.

   Presently, Assistant Professor of Chemistry, University of Hawaii

Table 3

Invited Seminars and papers presented

1. Exxon Research and Engineering, Clinton, NJ, November 1985.
2. Kansas State University, Manhattan, KS, October 1986
3. University of Pennsylvania, Philadelphia, November 1986.
4. IBM, T. J. Watson Research Center, Yorktown Heights, NY, November 1986.
5. Brookhaven National Laboratory, February 1987.
6. Fudan University, Shanghai, PRC, June 1987.
7. Peking University, Beijing, PRC, June 1987.
8. Symposium on Structure and Dynamics of Surfaces, ACS National Meeting, New Orleans, LA, September 1987.
9. Gordon Conference on Atomic and Molecular Interactions, August 1988.
10. Symposium on Cluster Interactions, ACS National Meeting, Boston, April 1990.

AFOSR-TR- 90-0122

COMPLETED PROJECT SUMMARY

TITLE: Mechanisms of Reactive Etching

PRINCIPAL INVESTIGATOR: Steven L. Bernasek
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INCLUSIVE DATES: 1 May 1985 - 30 June 1989

CONTRACT/GRANT NUMBER: AFOSR 85-0209G

COSTS AND FY SOURCE: $119,928, FY85; $119,678, FY86; $79,097, FY87; $68,510, FY 88; $65,000, FY 89.

SENIOR RESEARCH PERSONNEL: Dr. Che-Chen Chang

JUNIOR RESEARCH PERSONNEL: Alexander Robertson, Jr., Guo-Qin Xu
Richard J. Holland Michael Ruggio
Chih-Chen Cho Liang T. Chu

PUBLICATIONS:

1. "Thermal and Photochemical Promotion of Silicon Etching by Carbonyl Difluoride," R. J. Holland and S. L. Bernasek, J. Appl. Phys, 60, 2553 (1986).
2. "Summary Abstract: The Adsorption and Decomposition of Molybdenum Hexacarbonyl on Mo and Si Surfaces," J. Vac. Sci. Technol. A5, 1088 (1987).
3. "Stochastic Trajectory Studies of Small Argon Cluster Scattering from Pt(111)," G.-Q. Xu, S. L. Bernasek and J. C. Tully, J. Chem. Phys. 88, 3376 (1988).
4. "Experimental Studies of the Dynamics of Nitrogen Van der Waals Cluster Scattering from Metal Surfaces," R. J. Holland G.-Q. Xu, J. Levkoff, A. Robertson, Jr., and S. L. Bernasek, J. Chem. Phys. 88, 7952 (1988).
5. "UHV Transport System for Laser Irradiation Studies," A. L. Helms, Jr., W. A. Schiedt, S. L. Bernasek and B. M. Biwer, Rev. Sci. Instrum., 59, 1223 (1988).
6. "Dynamics of Cluster Scattering from Surfaces," G.-Q. Xu, R. J. Holland S. L. Bernasek and J. C. Tully, J. Chem. Phys., 90. 3831 (1989).
7. "Molybdenum Deposition from the Decomposiion of Molybdenum Hexacarbonyl," C. C. Cho and S. L. Bernasek, J. Appl. Phys. 65, 3035 (1989).
8. "Inelastic Scattering of N_2 from Fe(111)," M. Ruggio, L. Chu and S. L. Bernasek, Applied Physics A, in press.
9. "Translational Energy Dependent Scattering of N_2 from Fe(111): Angular and time-of-flight distribution measurements," L. Chu, M. Ruggio, and S. L. Bernasek, manuscript in preparation.
10. "Energy Dependent Scattering of CH_4 from Fe(111)," L. Chu, M. Ruggio, and S. L. Bernasek, manuscript in preparation.
11. "Design and Implementation of a Multiple Purpose Molecular Beam Surface Scattering Apparatus," L. Chu, A. Robertson, Jr., M. Ruggio, R. Holland, J. Levkoff and S. L. Bernasek, manuscript in preparation.

ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS

The objective of this research program was to investigate the mechanisms of the reactive etching of silicon and related aspects of the surface chemistry of electronic materials. Thermal and photochemical etching of Si(111) and SiO_2 surfaces by COF_2 was studied. A general purpose molecular beam surface scattering apparatus was constructed in order to investigate the mechanisms and dynamics of surface reaction processes.

The inelastic scattering of N_2 and CH_4 from the Fe(111) surface was studied using this instrument, and information about the gas-surface interaction potential for these systems extracted by comparison of the measurements with model calculations. The scattering of N_2 van der Waals clusters from solid surfaces was also investigated. The tangent peaked angular distributions and unusual rotational energy distributions of the scattered cluster fragments were interpreted by reference to stochastic trajectory calculations used to model the interaction. These studies have indicated mechanisms for the growth of high quality thin films from cluster beam sources.

Deposition of metallic thin films from organometallic precursors was also studied. Differences in film quality and composition were noted depending on whether thermal, electron beam, or photochemical methods were used to initiate the deposition.

AFOSR Program Manager: Lt. Col. Larry Burggraf